Saskatchewan
Research Council

# Preliminary Study of the Regional Distribution in the Atmosphere of the Vapour Phase of Widely Used Pesticides Within Western Canada

by
S.R. Shewchuk
K. Wallace

SRC Technical Report No. 210

Publication E-906-7-B-88 February, 1988

# PRELIMINARY STUDY OF THE REGIONAL DISTRIBUTION IN THE ATMOSPHERE OF THE VAPOUR PHASE OF WIDELY USED PESTICIDES WITHIN WESTERN CANADA

by

S.R. Shewchuk
K. Wallace

SRC Technical Report No. 210

SRC Publication No. E-906-7-B-88

February, 1988

**SUMMARY**

This project was designed to monitor the regional quality of the air of western Canada for pesticides. The common pesticides used by the agricultural community provided the central focus for this research. Special care was taken to ensure that local contamination effects were minimized on the sampler and that USEPA approved procedures for monitoring pesticides in the air were used.

Samples were collected monthly from the five month period June to October, 1987. No pesticides were observed in the ambient atmosphere within the detection limits of the observing system.

**ACKNOWLEDGEMENTS**

This research project was undertaken for Environment Canada on contract serial number KM531-7-0328/01-SGX during the 1987 field season. The scientific authority for the work was Mr. D.G. Schaefer, Chief, Scientific Services Division, Atmospheric Environment Service (Central Region). The authors would like to sincerely thank Mr. Schaefer for his continued interest and assistance in conducting this work. His comments and guidance proved most helpful in initiating and directing this research project.

We would also like to thank Dr. R. Grover, Section Head, Herbicide Behaviour in the Environment Section and Mr. L.A. Kerr of Agriculture Canada, Research Station, Regina, Saskatchewan. The Agriculture Canada personnel were most helpful in providing technical assistance in the methodology and design of the sampling and extraction system.

Field projects such as this one would have no chance for success if it was not for dedicated and interested field observers. We have had excellent cooperation from the field personnel at Rock Point (Mr. T. Tuomi) and Cree Lake (Mr. T. Layes), Saskatchewan on this project.

Technical assistance was provided by a series of Saskatchewan Research Council (SRC) staff members. We most especially would like to acknowledge the contribution of Dr. W. Yuen, M. Fahri, D. Diduck, and R. Jahren. Special thanks are due also to the personnel of the National Research Council, Mass Spectrometer Laboratory for assisting in the confirmations.

# TABLE OF CONTENTS


| | Page |
|---|---|
| SUMMARY | i |
| ACKNOWLEDGEMENTS | ii |
| LIST OF FIGURES | iv |
| LIST OF TABLES | iv |
| INTRODUCTION | 1 |
| Pesticides in the Air of Western Canada | 1 |
| Objective of this Study | 2 |
| The Study Area | 2 |
| The Pesticides | 4 |
| MATERIALS AND METHODS | 5 |
| The PS-1 Sampler | 5 |
| PUF Extraction and Analysis Procedures | 8 |
| Electron Capture Gas Chromatograph Analysis | 9 |
| The Gas Chromatography/Mass Spectrum Analysis | 10 |
| RESULTS | 12 |
| The PUF-XAD-2 Plug Verification | 12 |
| Field Results | 13 |
| DISCUSSION | 16 |
| RECOMMENDATIONS | 17 |
| REFERENCES | 19 |
| APPENDIX I - GAS CHROMATOGRAPH RESULTS. | 21 |
| APPENDIX II - THE CCAI COLLECTOR. | 25 |

## LIST OF FIGURES


| Figure | | Page |
|---|---|---|
| 1 | The Location of the Monitoring Sites . . . . . | 3 |
| 2 | The PS-1 Sampler . . . . . | 6 |
| 3 | The PUF Cartridge Holder . . . . . | 7 |
| 4 | The GC Trace a) The Rock Point Sample; b) Selected Standard Pesticides . . . . . | 15 |


## LIST OF TABLES


| Table | | Page |
|---|---|---|
| 1 | Commonly Used Pesticides in Western Canada . . . . . | 4 |
| 2 | Average Pesticide Recoveries (%) from Spiked PUF-XAD-2 Plugs . . . . . | 12 |
| 3 | Total Pesticide Mass Found on the PUF Plugs at Rock Point . | 13 |

## INTRODUCTION

### Pesticides in the Air of Western Canada

Each year significant amounts of pesticides are applied to the agricultural lands of western Canada. There are more than 17 million kilograms of herbicides used in western Canada annually (Manitoba Department of Agriculture 1984). Residues of these pesticides are known to enter the atmosphere on dust particles and by volatilization from soil and water surfaces. Thus they have the potential of travelling over great distances. Cohen and Pinkerton (1966), for example, traced the 2000 km movement of a dust cloud from an agricultural area in western Texas to Cincinnati, Ohio.

Pesticides are primarily applied either by groundrig or aircraft sprayers. From these spraying operations the pesticide can enter the atmosphere as a contaminant either as a direct droplet drift or by post application volatility. The droplet drift process has been studied extensively at the Saskatchewan Research Council (SRC) by Maybank et al. (1978) who found that between 1 and 8% of the applied mass can be lost to the atmosphere for groundrig application and between 20 to 35% with aircraft spraying. The post application volatility process has been studied recently at Agriculture Canada by Grover et al. (1985) who found that as much as 20.8% of the applied mass of some commonly used herbicides (2,4-D) can be returned to the atmosphere in the vapour phase. Grover (1981, 1986) also has shown that residues of pre-emergence herbicides, such as triallate and trifluralin, were present in the air throughout the growing season. However, Shewchuk (1983) monitored the ambient air in Saskatchewan specifically for 2,4-D, a post emergent herbicide, over the spraying season, but no detectable amounts were found.

The former studies were focused primarily on the translocation of pesticides from an agricultural spraying operation while the latter studies were conducted to monitor the regional concentration of pesticides in the air at a non-agricultural site.

## Objective of this Study

The objective of this study is to determine if these and other commonly used pesticides can be detected in the air mass of an agricultural area of the Canadian West. Site selection will be such that local spraying activity should have a minimal effect on the sampler.

## The Study Area

The samplers were located at Rock Point and Cree Lake, Saskatchewan (Figure 1). The Rock Point area of Saskatchewan was considered to be typical of an agricultural area. The background site for monitoring pesticides was set up at Cree Lake, Saskatchewan. Cree Lake is located in the Precambrian Shield area of western Canada. This site is far away from pesticide spray activity.

Site selection was an important component of this work. We desired a location that would be free of the local influence of spray activity. A large community pasture near Rock Point, Saskatchewan was chosen. A local water well on the land provided electrical power for the sampler. The community pasture was near some spray activity. Within a radius of 5 km of this site there is herbicide usage with approximately 60% pre-emergent and 40% post emergent types. One-half of the area within this 5 km radius is actively farmed.

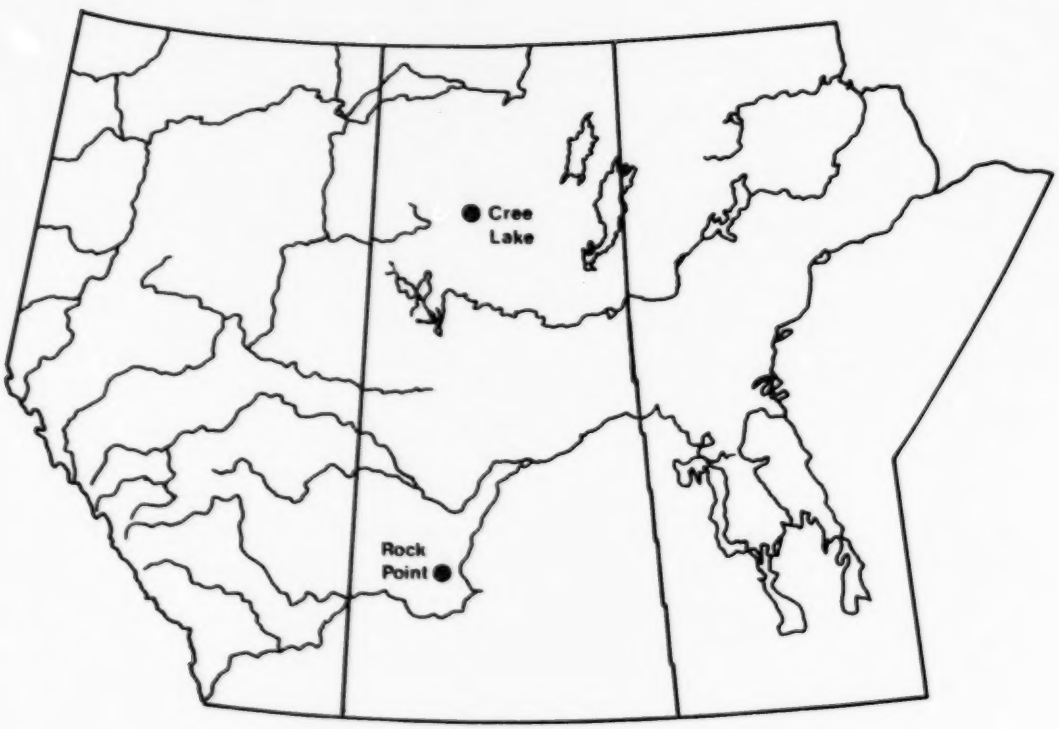



Figure 1. The Location of the Monitoring Sites.

## The Pesticides

The term pesticide used in this report consists of herbicides, insecticides, fungicides, etc. By far the largest type of pesticide used on the prairies are herbicides. Most insecticides are used on a spotty as required basis in isolated areas. Herbicide usage is broad in area coverage and large amounts are used. In this work a multi-residue analysis for common pesticides was conducted. A list of the pesticides is given in Table 1. The herbicides of 2,4-D and some of the wild oat herbicides (triallate and trifluralin) are the most heavily used. Herbicides such as 2,4-D and diclofop-methyl are post emergent. Herbicides such as triallate and trifluralin are pre-emergent types.

Table 1. Commonly Used Pesticides in Western Canada.

| Herbicides | Insecticides |
|---|---|
| triallate | dimethoate |
| trifluralin | lindane |
| diclofop-methyl | lorsban |
| 2,4-D | |
| MCPA | |
| dicamba | |
| bromoxynil | |

## MATERIALS AND METHODS

### The PS-1 Sampler

A PS-1 PUF (Poly Urethane Foam) sampler was located at each monitoring site. The sampler is seen in Figure 2. The PUF sampler is a complete air sampling system designed to collect airborne pesticide vapours at flow rates up to 280 L per minute. The sampler is a USEPA (1984) method of sampling for pesticides (Lewis et al. 1977). The sampler was operated daily during the period from 1:00 p.m. to 2:00 p.m. for the entire duration of the month. The flow rates (approximately 110 L/min.) were adjusted such that 200 $m^3$ of air were sampled per month. Since most pesticide fluxes from the soil occur in the early morning period during the formation of dew, the sampling of the air at that time is a possibility. However, during the morning periods the atmosphere is usually quite stable and not well mixed. It was felt, once the compounds are in the air, that the afternoon period, with a well mixed atmosphere, would provide the best opportunity to monitor the species.

Air enters the PS-1 unit and the particulates are trapped on a 10.16 cm diameter quartz filter paper (Whatman QM-A type). There is 25 g of XAD-2 resin in a sandwich between the plugs (Figure 3). The plugs and resin are supported by two 16 mesh stainless steel screens housed in a glass holder.

The samplers were installed at Rock Point and Cree Lake. At Rock Point the CCAI (Canadian Centre for Advanced Instrumentation) minitube air sampling system was collocated with the PS-1 sampler. The CCAI instrument collects organic compounds with a solid adsorber (usually Tenax) which allows direct injection (via thermal desorption) into a gas chromatograph (see the Appendix). It has a greater sensitivity than the

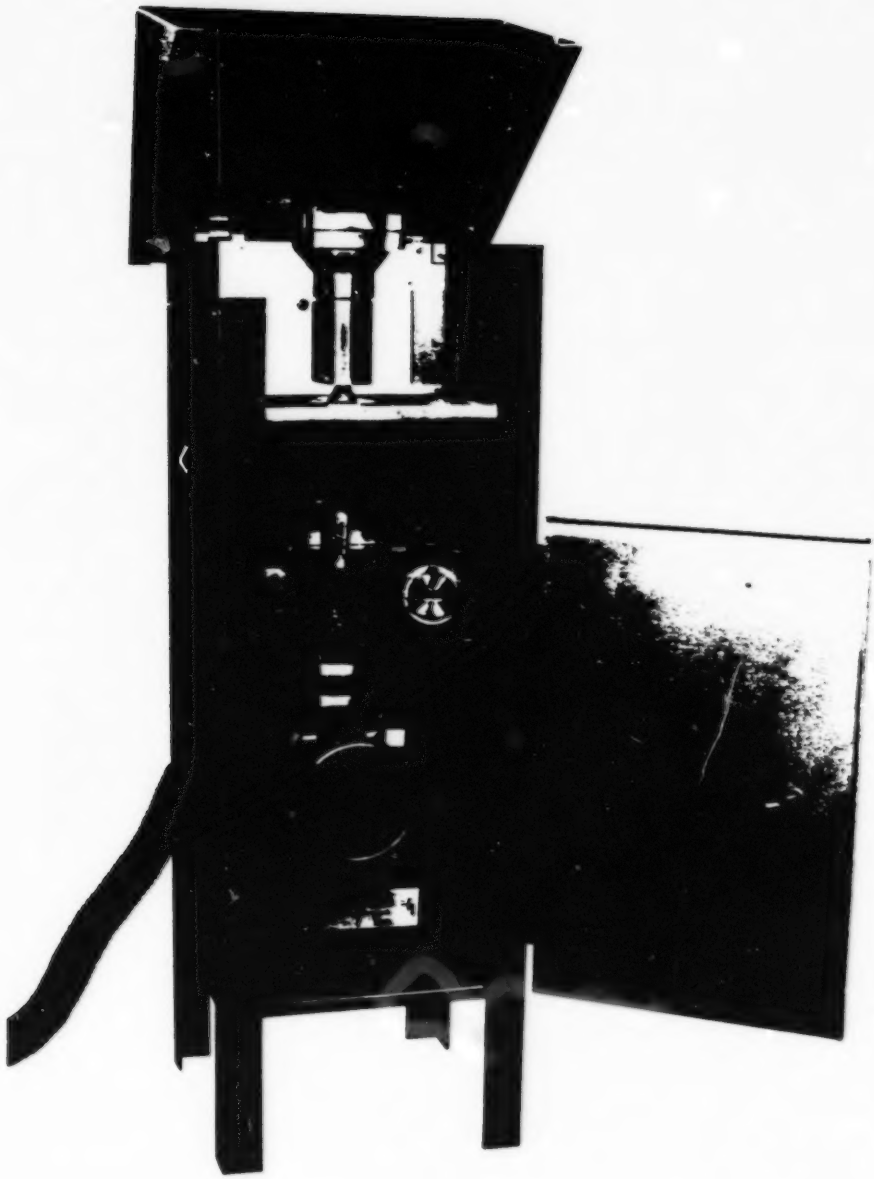


Figure 2. The PS-1 Sampler.

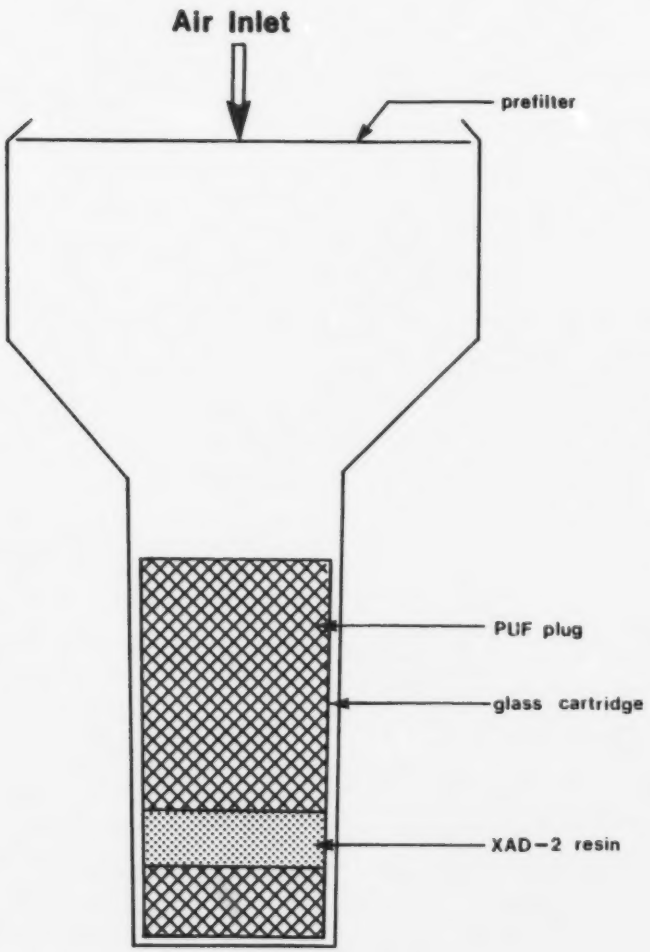



Figure 3. The PUF Cartridge Holder.

PS-1 PUF sampler. The minitube air sampler is a new innovation in pesticide sampler technology developed at the Saskatchewan Research Council. Daily samples (versus monthly for the PS-1 unit) of air were collected with the minitube sampler. This sampler was not considered part of this research contract. It was an instrument constructed for a separate project. This instrument was considered of possible interest for monitoring of herbicides. The material in the appendix is provided for information only.

PUF Extraction and Analysis Procedures

We have modified the PS-1 PUF plug to include a layer of XAD-2 resin. This resin is a granular solid media, which is used to extend the breakthrough volume for the selected pesticides. All exposed PUF plugs were kept in freezer storage at the site until the end of the field program then the samples were shipped in the frozen state to the SRC laboratories for analysis. The June Rock Point plug, however, was analyzed immediately after it was exposed. Once at the laboratory the plugs were immediately extracted and analyzed for pesticide.

All PUF plugs were extracted for 16 hours with 750 mL of pesticide grade acetone and hexane (50:50 mixture) in a soxhlet apparatus (USEPA 1984). The collected sample volume was reduced to 10 mL on a rotary evaporator at 35°C. The sample was analyzed directly by a gas chromatograph for the following pesticides: triallate, trifluralin, diclofop-methyl, bromoxynil, dimethoate, lindane and lorsban. A Hewlett Packard 5730A gas chromatograph was used with a megabore column (0.75 mm id, 30 m long, SPB-5 polarity). In order to analyze for 2,4-D, dicamba and MCPA a derivatization procedure (Lee and Chau 1983) was employed.

Carbofuran was analyzed using procedures from Environment Canada (1978).

The gas chromatograph was used initially for the sample analysis because this is the standard method of "quantifying" the amount of pesticides present. The common procedure is to conduct a gas chromatograph/mass spectrometer run to positively identify the compounds. The reason is that several compounds often can have the same retention time in the electron capture gas chromatograph.

Prior to transport and assembly in the field the PUF plug components were soxhlet extracted for 22 hours with acetone. This was done to ensure that they were sufficiently cleaned for the field. The PUF plugs and XAD-2 resin were then placed in the glass housing and soxhlet extracted for an additional 22 hours with acetone:hexane (50:50). The solvent was reduced in volume to 10 mL on a rotary evaporator at 35°C. A 1 microlitre aliquot was injected into a gas chromatograph Electron Capture Detector in order to check the sample purity. If no peaks were found that would interfere with the pesticides of interest then all the samples would be shipped to the field.

The actual field samples were extracted for 16 hours with 750 mL of pesticide grade acetone:hexane (50:50). Again the extract was reduced to 10 mL prior to analysis using a rotary evaporator at 35°C.

Electron Capture Gas Chromatograph Analysis

Pesticide samples were analyzed with a Hewlett Packard model 5730A Ni63 electron capture gas chromatograph. A 30 m SPB-5 polarity megabore column was used with a film thickness of 1.0 micron. The column temperature was 220°C then increased to 250°C at 4°C/minute. The detector and injector temperature were 300°C and 250°C respectively. The flow

rate of gas (90% methane and 10% argon) through the column was 5 mL/minute and the make up gas was at 30 mL/minute. A 1 microlitre aliquot was injected into the chromatograph. The estimated detection limits were 0.01 nanograms for lorsban, dimethoate, trifluralin and triallate and 0.005 ng for lindane. Diclofop-methyl and carbofuran gave detection limits of 0.05 ng, bromoxynil was 0.02 ng and MCPA, dicamba and 2,4-D were 0.01 ng. Integrations were performed on a Hewlett Packard model 3392 integration system.

Clean up was not necessary for residue samples prior to gas chromatograph analysis for lorsban, dimethoate, lindane, trifluralin, triallate, bromoxynil and diclofop-methyl. Dicamba, MCPA and 2,4-D were derivatized using the procedures of Lee and Chau (1983). The penta florulbenzyul bromide (PFBBR) ester was made in order to increase the sensitivity of the analyses. In the case of carbofuran a slightly different procedure is followed (Environment Canada 1978).

The Gas Chromatography/Mass Spectrum Analysis

A Finnigan model 4500 (electron impact positive ion) system was used interfaced to a Data General Nova 4X data system. The National Bureau of Standards Library of some 40,000 compounds is on file, in order to compare and identify unknown compounds. The library contains triallate (Avadex BW), trifluralin (Treflan), 2,4-D iso-octyl ester and dimethoate.

The running conditions were as follows:

| | |
|---|---|
| Injection Temperature | 70°C then up to 100°C |
| Column Temperature | 100-300°C at 10°C/minute, hold at 300°C until no peaks |
| Carrier Gas | High purity He at 40 cm/sec at 150°C |
| On Column Injection of 2 uL<br>Electron Energy | 70 ev (nominal) |
| Column | 60 m x 0.32 mm id fused silica capillary coated with SE-54 (DB-5) |
| Ion Source Temperature | 200°C |
| Separator/Analyzer Temperature | 280°C |

The detection limits of the system were in the order of 0.1-0.2 ng for the compounds of interest.

## RESULTS

### The PUF-XAD-2 Plug Verification

When a pesticide gets trapped in the PUF-XAD-2 plug, it may or may not remain on the plug because moving air has a tendency to pass the pesticide through the sampling system. Table 2 shows the spiked recovery rates from the PUF-XAD-2 adsorbing medium. Trifluralin, triallate and 2,4-D iso-octyl ester were applied onto the PUF-XAD-2 plugs with 10 micrograms of each compound and 12.8 micrograms of lorsban; the plugs were then extracted for 16 hours in a soxhlet apparatus. The recoveries ranged from 75% for trifluralin to 90% for lorsban. Lewis and MacLeod (1982) have suggested recoveries >75% represent efficient trapping of pesticides.

Table 2. Average Pesticide Recoveries (%) from Spiked PUF-XAD-2 Plugs.

| No. of Samples | Trifluralin* | Triallate | Lorsban | 2,4-D Iso-octyl Ester |
|---|---|---|---|---|
| 2 | 75 | 86 | 90 | 88 |

*Percent recovery based on 10 ug spike for trifluralin, triallate and 2,4-D and 12.8 ug for lorsban on plugs.

By aspirating a sufficient volume of air over a spiked amount of pesticide on the filter and tracing it through the sampler it is possible to move the species from the filter to the plug in varying amounts. The volume of air needed to remove a given fraction of the mass has been presented by Grover et al 1988. The retention efficiency of most PUF-XAD-2 units were in the order of 90% or more for most of the pesticides used in this project.

Field Results

The SRC laboratory results for the field exposed plugs at Rock Point and Cree Lake are shown in Appendix I. Table 3 is a summary of the results for the Rock Point sampling site only. It is seen that most pesticides of interest are below the detection limit. Detection limits

Table 3. Total Pesticide Mass Found on the PUF Plugs at Rock Point.

| Pesticide | June (ug) | July (ug) | August (ug) | September (ug) | October (ug) |
|---|---|---|---|---|---|
| trifluralin | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| dimethoate | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| lindane | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| triallate | 0.29* | <0.1 | <0.1 | <0.1 | <0.1 |
| lorsban | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| diclofop-methyl | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| bromoxynil | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| dicamba | <1 | <1 | <1 | <1 | <1 |
| MCPA | <1 | <1 | <1 | <1 | <1 |
| 2,4-D | <2 | <2 | <2 | <2 | <2 |
| carbofuran | <2 | <2 | <2 | <2 | <2 |

* Not confirmed by gas chromatograph mass spectrometer.

ranged from <2 to <0.05 micrograms per plug. There was one interesting sample in all the exposed PUF plugs that were analyzed. The June Rock Point plug showed a detectable amount of what was thought to be triallate. Figure 4 shows the gas chromatograph output trace for that PUF-XAD-2 plug. The peak at 8.17 minutes seems to indicate the presence of triallate. However, standard pesticide samples in the lower trace

indicate the presence of triallate at 8.13 minutes. Using only the electron capture gas chromatograph triallate seems to be present. However, the presence of the peak was not sufficiently definitive to identify triallate. A series of standards of triallate and other pesticides were run on the gas chromatograph/mass spectrometer of the National Research Council in subsequent confirmations. The peak on the electon capture gas chromatograph was confirmed not to be triallate by gas chromatograph/mass spectrometer analysis. In fact the peak thought to be triallate was actually a hydrocarbon, 6,10-dimethyl 2-undecanone. All other samples showed no presence of any of the gas chromatograph/mass spectrometer library pesticides.

The above hydrocarbon was one of a series of approximately one dozen low concentration hydrocarbon compounds found in the plug extract. All of these compounds are believed to be naturally occurring volatile organic substances (Altshuller, 1983).

The results for the CCAI minitube air sampling system were not available at the time of this report. These results will be published separately. The CCAI instrument was not part of this research contract.

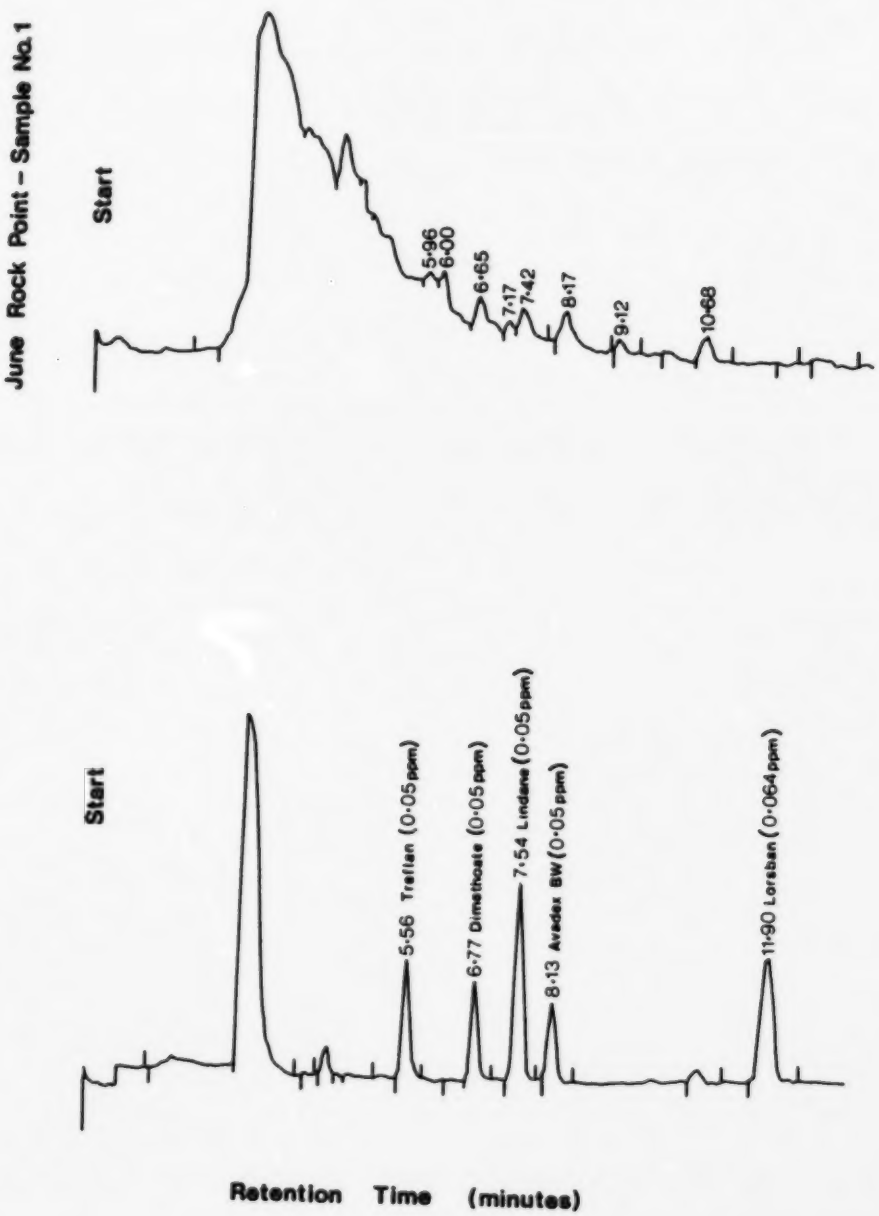



Figure 4. The GC Trace a) The Rock Point Sample;
b) Selected Standard Pesticides.

## DISCUSSION

No pesticides were found in the environment in the target area (Rock Point) or in the background area (Cree Lake) with this approved pesticides in the air monitoring device. It is difficult to draw generalizations from this research, but we feel that the ambient contamination of the air from pesticide usage in western Canada is primarily a local site specific one.

Pesticides may be found in and around the site of local spray operations with instruments similar to what was used in this project. However, the atmospheres rapid dispersive power is sufficiently great such that the concentrations are below the detection limit capability of the monitors used in this project ($<0.5$ ng/$m^3$) averaged over a monthly period. If more air volumes ($>200$ $m^3$) and the influence of oxidants were more fully understood, it would be possible to extend the detection limits of this instrument.

**RECOMMENDATIONS**

1. There is significant concern for dust in the air as a major translocation vehicle for dust (Grover et al 1988). This is so because pesticides such as triallate and treflan are strongly adsorbed to soil particles. The upper driftable layers of soil are most prone to wind erosion and to the presence of pesticides. **It is recommended that future studies on regional and long range transport of pesticides in the environment focus on dust in the air.** The frequency and severity of dust storms in western Canada should be investigated along with monitoring programs to quantify dust transport and to determine possible pesticide translocation to prairie water sheds and wet lands by way of this vehicle. In addition, atmospheric dust acts as condensation nuclei for cloud particles. This, coupled with normal wash out and rain out processes in precipitating cloud systems, likely results in pesticide contamination of rain water.

2. It remains of considerable interest to monitor and understand the transport pathway about local application sites in western Canada. During the peak spray season (late May-mid June) it may be appropriate to take daily (24 hour) air samples with the PS-1 monitor to fully understand the environmental impacts. Studies of this nature must continue to be conducted on a pesticide by pesticide basis because each species has significantly different physical properties that make its behavior to the atmosphere as a flux difficult to predict. **It is recommended that programs continue to monitor and understand the atmospheric transport pathway about local application sites.**

3. Many of the problems associated with trapping of the specific pesticides identified in the study in the PUF plug should be more fully

researched in laboratory programs. While the effect of pesticide breakthrough was effectively considered in this project and others, the influence of oxidation products and in situ pesticide degradation on the trapped molecules has not been fully considered in projects to the present. **It is recommended that research activity continue to modify and improve the PS-1 samples for monitoring pesticides of interest in western Canada.**

## REFERENCES

Altshuller, A.P. 1983. Review: Natural Volatile Organic Substances and Their Effect on Air Quality in the United States. Atmospheric Environment 17, (11), pp. 2131-2165.

Cohen, J.M. and C. Pinkerton. 1966. Widespread Translocation of Pesticides by Air Transport and Rain-out. Advanced in Chemistry 60, pp. 163-182.

Environment Canada. 1978. Analytical Manual for N-methyl Carbaniates in Water. Publication No. 18574.

Grover, R., L.A. Kerr and S.U. Khan. 1981. Multidetector Gas Chromatographic Determination of Confirmation of Airborne Triallate Residues in Saskatchewan. Journal Agriculture and Food Chemistry 29, pp. 1082-1088.

Grover, R., S.R. Shewchuk, A.J. Cessna, A.E. Smith and J.H. Hunter. 1985. Fate of 2,4-D Iso-octyl Ester After Application to a Wheat Field. J. Environmental Quality 14, pp. 203-210.

Grover, R. 1986. Magnitude and Source of Airborne Residues of Herbicides in Saskatchewan. In: J.A. Djosman (Ed.), International Symposium on "Health and Safety in Agriculture". Academic Press, New York, NY.

Grover, R., L.A. Kerr and D. Lintott. 1988. Personal communication.

Lee, H.B. and A.S. Chau. 1983. Analysis of Pesticide Residues by Chemical Derivatization VI. Analysis of Ten Acid Herbicides in Sediment. J. Assoc. Off. Anal, Chem. Vol. 66, No. 4, pp. 1023-1028.

Lewis, R.G., A.R. Brown, K.E. MacLeod and M.D. Jackson. 1977. Evaluation of Polyurethane Foam for Sampling of Pesticides, Polychorinated Biphenyls and Polychlorinated Naphthalenes in Ambient Air. Analytical Chemistry 49, pp. 1668-1672.

Lewis, R.G. and K.E. MacLeod. 1982. Portable Sampler for Pesticides and Semivolitile Industrial Organic Chemicals in Air. 1982. Analytical Chemistry 54, pp 310-315.

Manitoba Department of Agriculture. 1984. Herbicide Use Survey, Statistics Section.

Maybank, J.M., K. Yoshida and R. Grover. 1978. Spray Drift from Agricultural Pesticide Applications. APCA J. 28:1009-1014.

Shewchuk, S.R. 1983. Continuous Ambient Monitoring of Trace Levels of Organic Pesticide. SRC Publication No. E-906-1-B-83, SRC Technical Report No. 142.

USEPA. 1984. Method for the Determination of Organochlorine Pesticides and Polychlorinated Byphenyls in the Ambient Air, Method TO4. Revision 1.0 April.

# APPENDIX I

## GAS CHROMATOGRAPH RESULTS

Mass in ug from the June Rock Point PUF-XAD-2 Plug.

| | |
|---|---|
| Trifluralin: | <0.1 |
| Dimethoate: | <0.1 |
| Lindane: | <0.05 |
| Triallate: | 0.29* |
| Chlorpyrifos: | <0.1 |
| Diclofop-methyl: | <0.5 |
| Bromoxynil: | <0.2 |
| Dicamba: | <1 |
| MCPA: | <1 |
| 2,4-D: | <2 |
| Carbofuran: | <2 |

* not confirmed by gas chromatograph mass spectrometer analysis

# SASKATCHEWAN RESEARCH COUNCIL
## ANALYTICAL SERVICES

Environment Sector, SRC
15 Innovation Blvd.
Saskatoon, Saskatchewan S7N 2X8
Attn: K. Wallace, E906-18

JAN 18 '88

Date Samples Received: 02-Dec-87 Client P.O.:

SAMPLE CLIENT DESCRIPTION
12643 ROCK POINT #2 JULY *LIQUID*
12644 ROCK POINT #3 AUGUST *LIQUID*
12645 ROCK POINT #4 SEPT. *LIQUID*
12646 ROCK POINT #5 OCT. *LIQUID*

| ANALYTE | UNITS | ESQUA# | 12643 | 12644 | 12645 | 12646 |
|---|---|---|---|---|---|---|
| GLC Time Charge | -- | no-val | SEE BELOW | SEE BELOW | SEE BELOW | SEE BELOW |

| Analyte | units | #12643 | #12644 | #12645 | #12646 |
|---|---|---|---|---|---|
| Trifluralin | ug | <0.1 | <0.1 | <0.1 | <0.1 |
| Dimethoate | ug | <0.1 | <0.1 | <0.1 | <0.1 |
| Lindane | ug | <0.05 | <0.05 | <0.05 | <0.05 |
| Triallate | ug | <0.1 | <0.1 | <0.1 | <0.1 |
| Chlorpyrifos | ug | <0.1 | <0.1 | <0.1 | <0.1 |
| Bromoxynil | ug | <0.2 | <0.2 | <0.2 | <0.2 |
| Diclofop-methyl | ug | <0.5 | <0.5 | <0.5 | <0.5 |
| Dicamba | ug | <0.5 | <0.5 | <0.5 | <0.5 |
| MCPA | ug | <0.5 | <0.5 | <0.5 | <0.5 |
| 2,4-D(Iso-Octyl) | ug | <0.5 | <0.5 | <0.5 | <0.5 |
| Carbofuran | ug | <2 | <2 | <2 | <2 |

# SASKATCHEWAN RESEARCH COUNCIL
## ANALYTICAL SERVICES

Environment Sector, SRC
15 Innovation Blvd.
Saskatoon, Saskatchewan S7N 2X8
Attn: K. Wallace, E906-18

JAN 18 '88

Date Samples Received: 02-Dec-87 Client P.O.:

SAMPLE CLIENT DESCRIPTION
12638 CREE LAKE #1 JUNE *LIQUID*
12639 CREE LAKE #2 JULY *LIQUID*
12640 CREE LAKE #3 AUGUST *LIQUID*
12641 CREE LAKE #4 SEPT. *LIQUID*

| ANALYTE | UNITS | ESQUA* | 12638 | 12639 | 12640 | 12641 |
|---|---|---|---|---|---|---|
| GLC Time Charge | -- | no-val | SEE BELOW | SEE BELOW | SEE BELOW | SEE BELOW |

SAMPLE CLIENT DESCRIPTION
12642 CREE LAKE #5 OCT. *LIQUID*

| ANALYTE | UNITS | ESQUA* | 12642 |
|---|---|---|---|
| GLC Time Charge | -- | no-val | SEE BELOW |

| Analyte | units | #12638 | #12639 | #12640 | #12641 | #12642 |
|---|---|---|---|---|---|---|
| Trifluralin | ug | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Dimethoate | ug | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Lindane | ug | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| Triallate | ug | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Chlorpyrifos | ug | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Bromoxynil | ug | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| Diclofop-methyl | ug | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| Dicamba | ug | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| MCPA | ug | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| 2,4-D(Iso-Octyl) | ug | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| Carbofuran | ug | <2 | <2 | <2 | <2 | <2 |

## APPENDIX II

## THE CCAI COLLECTOR

(Not part of this research contract)

**CANADIAN CENTRE FOR ADVANCED INSTRUMENTATION**

15 Innovation Blvd. Saskatoon Saskatchewan Canada S7N 2X8 Phone (306) 933-7066 Envoy: CCAI Telex: 074-2484

# MINITUBE™ Air Sampling System

## System Construction

A number of field-based microprocessor-controlled samplers make up the collection system while a modified gas chromatograph performs the analysis (Figure 1).

Air samples are taken by pumping air to be sampled through a minitube containing a polymer adsorber. Each field sampler is fitted with a carousel housing 50 minitubes.

A program module containing a library of 5 complete, 50 sample programs, in each sampler controller manages the selection, sampling time and flow rate. One controller can control up to 10 field samplers. Program modules are easily changed in the field within minutes.

The sampling process can be initiated either locally, with a hand-held switch or remotely by radio transmitter.

Once sampling is completed the carousel containing the minitubes is removed from the field sampler and taken to a laboratory for analysis by thermal desorption of the adsorbed contaminants in a gas chromatograph.

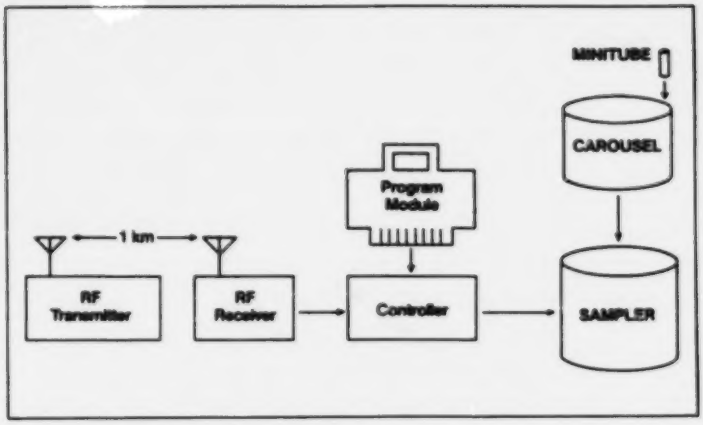



Figure 1 MINITUBE AIR SAMPLING STATION

## Simplified Analysis

Analysis is supported by an automated thermal desorption sample injection system that is retrofitted to a commercial gas chromatograph (Figure 2).

Control of the analysis cycle can be manually programmed by an operator through a front panel console or, optionally, through a preprogrammed module which can be plugged into the injection system.

The technique of thermal desorption permits reuse of the minitubes as contaminants are "flushed out" during analysis. The carousel can be removed from the injection system and immediately replaced in a field sampler for another sampling cycle.

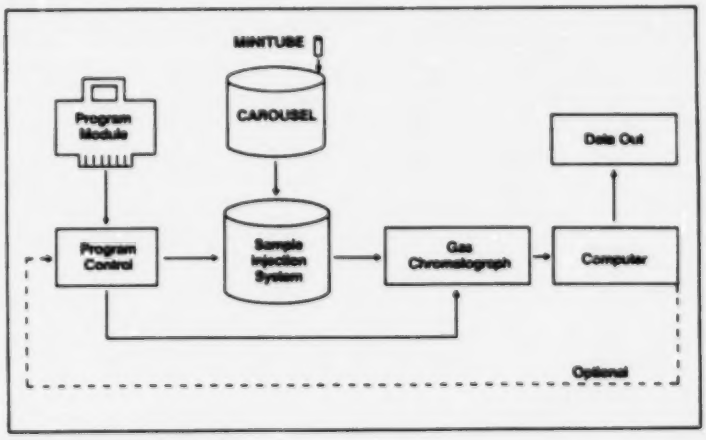
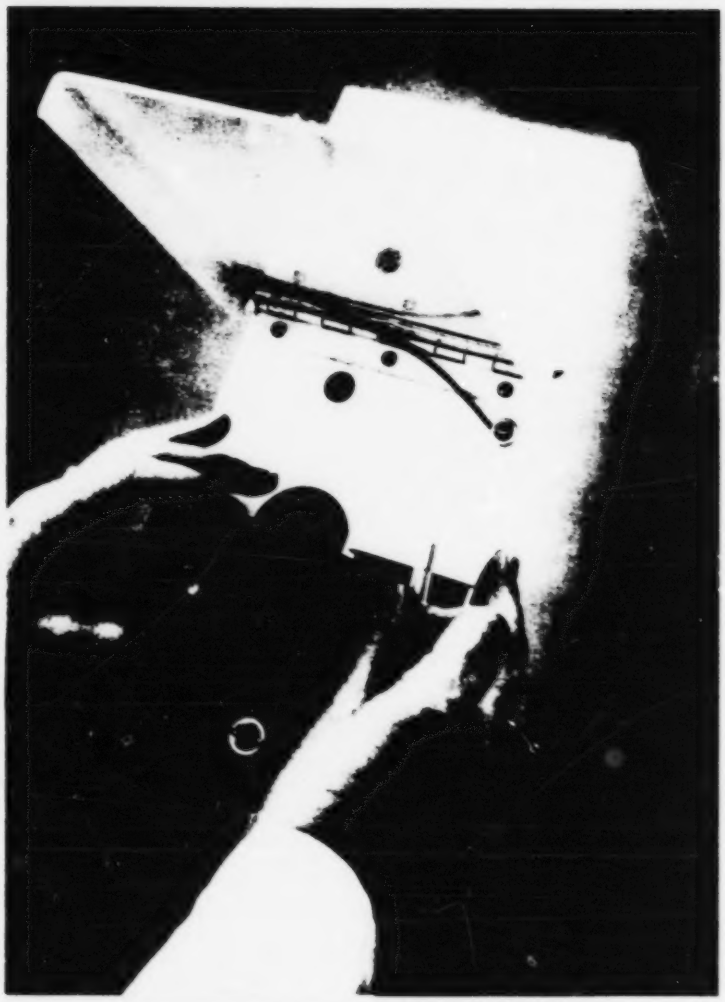



Figure 2 LABORATORY ANALYSIS

# MINITUBE™ Air Sampling System

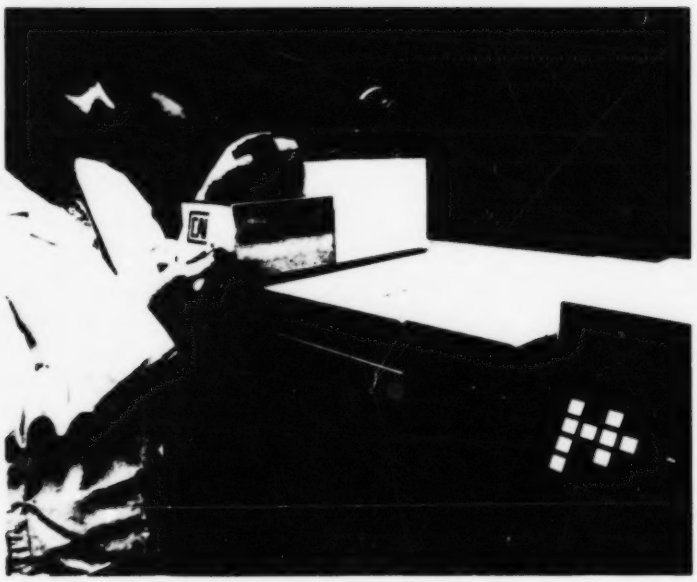
## A preprogrammed and automated system used to trap, collect, and analyze airborne contaminants in the form of gases, vapors, and aerosols

- **Cost effective** fully automated system reduces operator error and minimizes servicing
- a maximum of 10 field samplers may be operated from a single controller
- sampling process initiated remotely, by radio transmitter, or locally, with hand-held switch
- analysis facilitated by an automated thermal desorption unit retro-fitted to a commercial gas chromatograph
- a wide range of sampling parameters permits sampling of concentration extremes



CAI

CANADIAN CENTRE FOR ADVANCED INSTRUMENTATION



## Suggested Military Applications of MINITUBE™ Air Sampling System

1. Sampling/analysis of ambient air inside military collective protection systems to evaluate integrity against ingress of chemical warfare agents.

2. Air sampling/analysis in support of outdoor field trials to determine downwind hazard from explosively-disseminated or sprayed chemical warfare agents and simulants.

3. Air sampling/analysis of vapour evolving from liquid-contaminated surfaces to determine extent of contamination, contact hazard and effectiveness of decontaminants in removing contamination (e.g. CW agents). Such surfaces include vehicles, tentage, runways, aircraft and roadways.

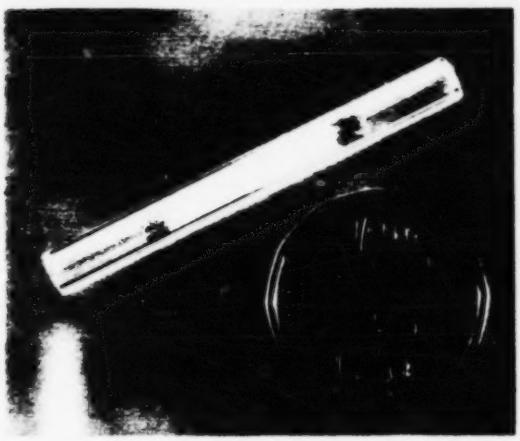
4. Air sampling/collection/analysis to detect and confirm the suspected use of toxic agents in battlefield environments. Timely collection and analysis of known and unknown agents assists in determining the type and extent of protective measures which must be taken to counteract the usage of such agents.

5. Breath analysis as a means of detecting the presence of drugs and their metabolites which could affect human performance under stressful situations.

6. Monitoring workplace air quality to ensure workers safety, (e.g. chemical storage areas, ammunition depots).

## Designed with the Canadian Department of National Defence

The tested and proven system is a product of the Canadian Centre for Advanced Instrumentation (CCAI), designed in cooperation with scientists from the Canadian Department of National Defence. The MINITUBE™ Air Sampling System replaces bubblers and manual analysis, a system found time consuming and restrictive in terms of overall analysis.



**Typical specifications**

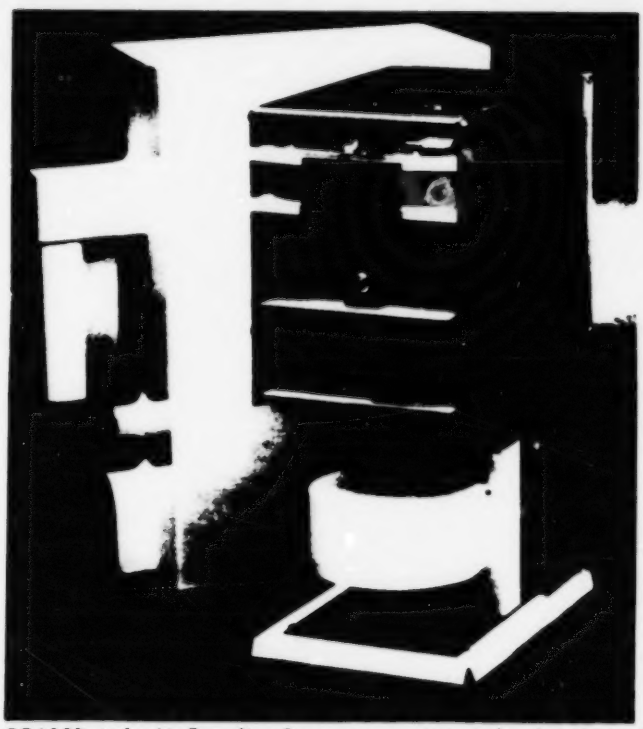
(Sampler with Controller) •
**Power:** AC Power (115 VAC/230 VAC) with battery back up or stand alone battery powered
**Ambient Temperature Range:** -5°C to 40°C
**Carousel Capacity:** 50 Samples
**Flow Rate Range:** 50 to 100 ml per minute
**Sample time:** seconds to hours
**Minimum Dead Time Between Samples:** 5 seconds
**Sampler Size:** 33 cm x 23 cm x 13 cm

• System can be customized to your specifications.

For additional information contact
Canadian Centre for
Advanced Instrumentation
15 Innovation Blvd.
Saskatoon, Saskatchewan
S7N 2X8
Telephone: (306) 933-7066
Telex: SARECO 074-2484

# CCAI NEWS

# CCAI invents the first, efficient Minitube Air Sampling System*



*CCAI Minitube Air Sampling System: preprogrammed and automated*

The Canadian Centre for Advanced Instrumentation, in cooperation with scientists from the Department of National Defence, has developed an automated air sampling system that will efficiently trap and collect airborne contaminants in the form of gases, vapors and aerosols, and subsequently analyze the collected contaminants.

The system consists of a number of field-based microprocessor-controlled samplers and a specially modified gas chromatograph to perform the analysis.

Air samples are taken by pumping the air to be sampled through a minitube containing a polymer adsorber. Each field sampler is fitted with a carousel housing fifty minitubes. A program module in each sampler controls the selection, sampling time, and flow rate. Program modules can be easily changed in the field.

After sampling is completed, the carousel containing the minitubes is removed from the field sampler and transported to the laboratory for analysis by chromatograph. Or, the carousel can be shipped to the Saskatchewan Research Council in Saskatoon, Saskatchewan for analysis on a fee-for-service basis.

*(*PATENT APPLIED FOR)*

## System seen to have many practical applications

Originally developed for the Canadian Department of National Defence as a means of confirming the use of toxic materials in battlefield situations, CCAI now sees a host of other applications for this unique system, including:

### For Agricultural and Environmental

Trace and measure quantities of airborne herbicides downwind of a crop spraying operation to determine the spread of herbicides.

### For Industrial Companies and Environmentalists

Collect and analyze effluents from industrial processes to investigate compliance with air quality standards.

### Industrial and Environmental Use

Monitor workplace air quality with respect to workers' health and safety concerns.

## Unique Features save time and money

Because the system is completely preprogrammed and automated, there's very little chance for operator error.

The system requires no technical expertise to operate, so anyone can do it. All an operator does is place the carousel inside the sampler and turn it on. After the samples are taken, the operator removes the carousel for analysis by one of the methods described above.

Low maintenance is also a big plus minimizing operating costs and downtime.

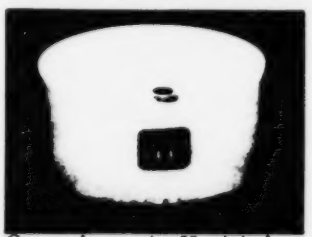
## Alternative Methods of Analysis:

**All methods require a gas chromatograph.**

1. A CCAI automatic preprogrammed thermal desorbtion valve is available to fit most commercial chromatographs. This method permits fully automated analysis.

2. Use manual techniques (solvent extraction or thermal desorbtion).

3. Send collected samples to the Saskatchewan Research Council for analysis.



*Carousel: capacity 50 minitubes*

## Typical Specifications

(Sampler with Controller)**
Power: AC power and or battery-operated
Ambient Temperature Range: -5° C to 40° C
Carousel Capacity: 50 Samples
Flow Rate Range: 50 to 100 ml per minute
Sample Time: seconds to hours
Minimum Dead Time Between Samples: 5 seconds
Sampler Size: 33 cm x 23 cm x 13 cm

***System can be customized to your specifications*

**For additional information contact:**
Don Barnett, Director CCAI
(306) 664-7066
30 Campus Drive
Saskatoon, Saskatchewan
S7N 0X1

CANADIAN CENTRE FOR ADVANCED INSTRUMENTATION

# CANADIAN CENTRE FOR ADVANCED INSTRUMENTATION

## Electronics and Computer Technology — Precision Instrumentation

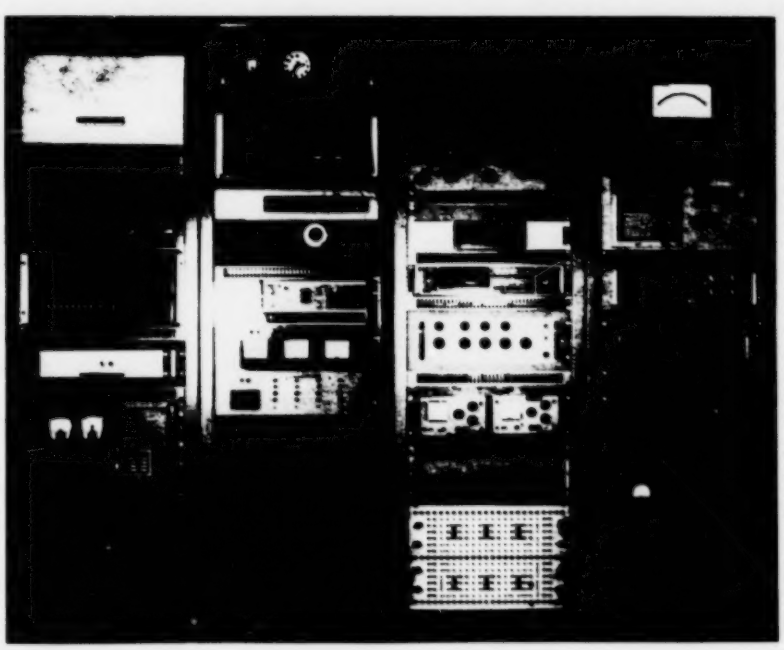
- 20 years of electronics, computer and instrumentation experience has led to the creation of CCAI and serves as the basis for its present scope of activities.
- Experienced, capable, innovative CCAI personnel offer a comprehensive service to their clients. They will help to define their client's goals and to find solutions to their client's instrumentation problems.
- Close liaison and co-operation with other instrumentation and systems groups and technologists, both on and off university campus, make CCAI unique in its knowledge and experience.
- The highly qualified staff has the capabilities and facilities to work in analog and digital electronics, electromechanical and electro-optical instrumentation, monitoring, systems analysis and design, computer software, microprocessor-based instruments, and product development.

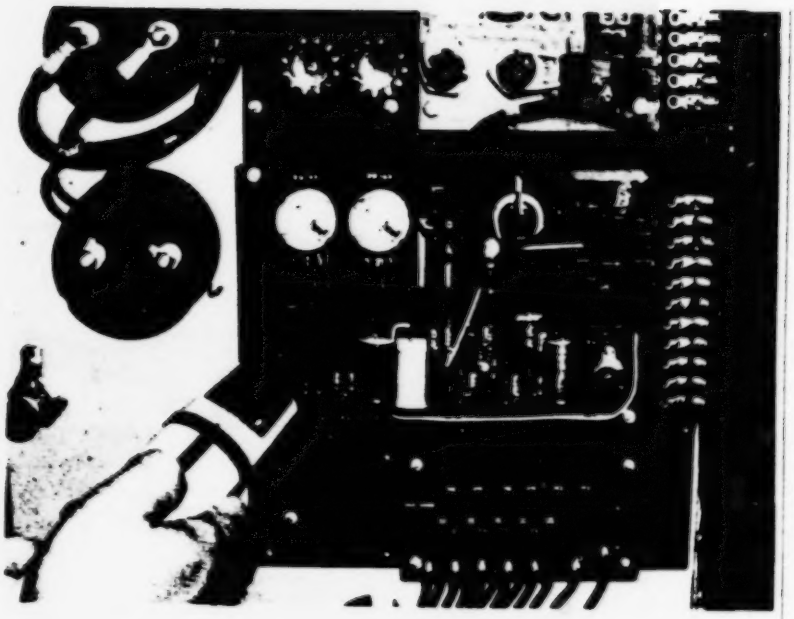
## Instrumentation Concept and Design

- On a contractual basis, either independently or in consultation with the client, CCAI will design a device or system to meet the specific instrumentation needs of the client.
- From the initial task of conceptualizing the proposed equipment to drawing up specifications, objectivity in judgement is maintained. CCAI is not committed to a particular product or procedure. Because each project varies in complexity and scope, it is the philosophy of CCAI to treat independently each of the carefully defined steps that are crucial to the development and success of the equipment.

## Prototype Development and Testing

- Before CCAI begins work on a prototype, a program to demonstrate the technical feasibility and market niche for the instrument is undertaken.
- A test bench is set up to try different approaches and various ideas in an attempt to gain the best possible solution to the problem.
- A prototype, which resembles the finished manufactured product in engineering and construction, is fabricated, studied, and tested for reliability, safety, compatibility with its proposed environment, and for ease and convenience of operation.





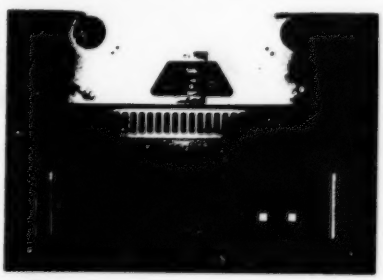
## Instrumentation, Fabrication and Manufacturing

- CCAI has the capabilities and facilities necessary to fabricate and manufacture small quantities of specialized instrumentation. This service is especially useful to small companies, hospitals, and some government agencies that do not have their own manufacturing capabilites.
- If the client's resources include the facilities to manufacture the equipment, the specifications, prototype, drawings, software, and any other pertinent material are turned over to him. CCAI will continue to be available to act as a consultant during the manufacturing process.
- On the request of the client, CCAI will locate a Canadian company interested in undertaking the manufacture of large quantities of the newly-designed equipment.
- CCAI will undertake one or all the steps towards the creation and production of specialized electronic equipment and advanced instrumentation, depending on the client's wishes and resources. In consultation with the client, CCAI will assist in every stage in the development of the new product.
- All steps and every stage of design and development are kept fully confidential.

## Continued Service, Maintenance, Repair and Calibration

- CCAI routinely performs the necessary service and repair of electronic instrumentation, and precision instruments of a mechanical nature. Whether the instrument has been manufactured by CCAI or manufactured commercially, CCAI personnel are knowledgeable and have the most up-to-date information on instrumentation technology available.
- From trouble-shooting and repair to calibration and testing, CCAI offers a complete follow-up service.
- If necessary, back-up experience and expertise is available from Saskatchewan Research Council's large professional and technical staff.

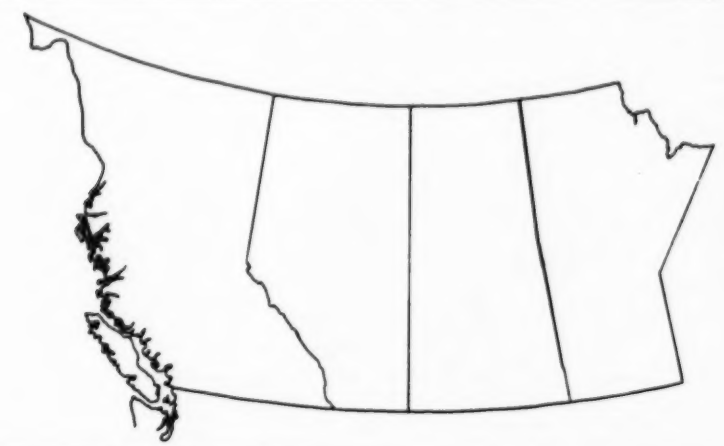
Contact:
D.B. Barnett, Director



**CANADIAN CENTRE FOR ADVANCED INSTRUMENTATION**

30 Campus Drive, Saskatoon
Saskatchewan, Canada S7N 0X1
Phone (306) 664-7066

CANADIAN CENTRE FOR ADVANCED INSTRUMENTATION



SASKATCHEWAN

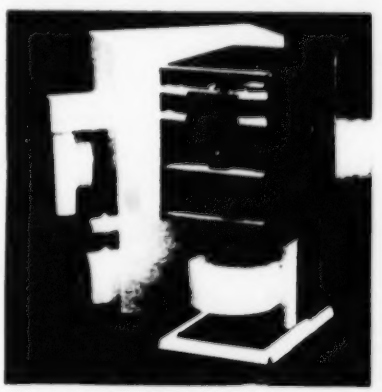
# Minitube sampling system fits different applications

The Minitube Air Sampling System (MASS) was designed and developed by the Saskatchewan Research Council's Canadian Centre for Advanced Instrumentation (CCAI) under contract to the Canadian Department of National Defence (DND). CCAI is a resource centre devoted to solving problems in industry, education and government through the use of innovative instrumentation.

Contact with DND's Defence Research Establishment in Suffield, Alberta (DRES) was made through the Head of SRC's Physics Division, a former Defence Research Establishment employee. Negotiations for the contract began in 1980 with the contract being awarded in 1982. DRES had some familiarity with the expertise available from CCAI through a previous small contract (the construction of a specialized injection valve for gas chromatography).

Field trials are conducted at Suffield to investigate the dispersion of aerosols of biological simulants over land areas of typically, one square kilometre. To do this effectively, upward of thousands of samples are required for each trial. To compound the measurement problem, aerosol concentrations over the test area vary by several orders of magnitude. Previous techniques to cope with this problem were cumbersome, unreliable and labor intensive. The obvious solution was a fully automated sampling system.

A working relationship was established between scientists at DRES and CCAI engineers and, after numerous discussions, a design was conceived and the Minitube Air Sampling System was born. A contract for $235,495 to develop a prototype system over 20 months was received in April, 1982.



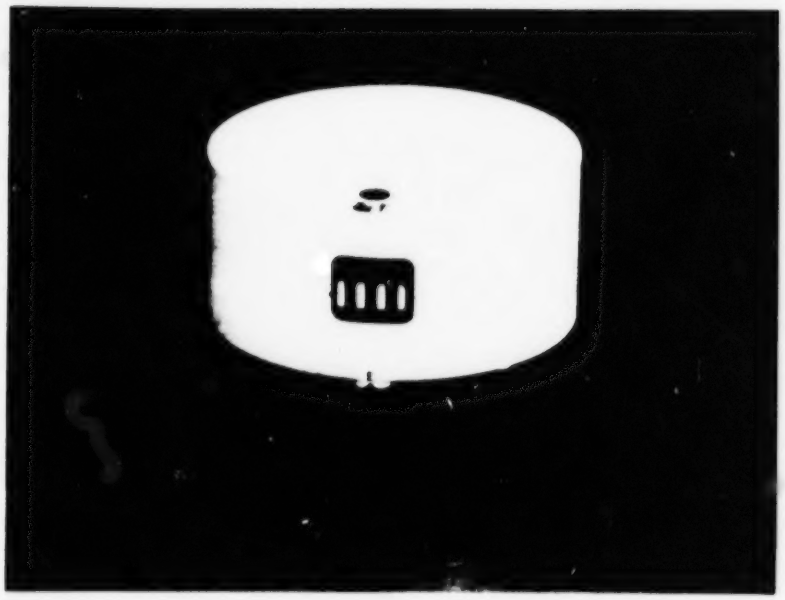
*A model of the field sampler.*

The resulting system is based on miniature reuseable sample tubes packed with a selected porous adsorbent (minitube). Air samples are drawn through the minitubes in the field and subsequently analyzed in the laboratory by gas chromatography techniques. The minitube is a glass tube, 38 mm long with an internal diameter of 2 mm and packed with approximately 15 to 20 mg of suitable adsorbent (e.g., Tenax GC).

A molded carousel houses 50 minitubes and is the transfer vehicle for the samples. When sampling occurs, only one tube at a time has air drawn through it with the other tubes being protected from cross-contamination. The design of the carousel permits collection and analysis to be performed without manually handling or sorting individual minitubes.

To correlate analysis to sampling, it is necessary to control the following parameters: flow rate of gas drawn through the adsorbent, sampling time period and the time of the event. All of these parameters are preprogrammed and stored in a program module. The program module is plugged into a microprocessor-based controller which, in turn, guides the field sampler through 50 sampling events. The controller is designed to control up to 10 field samplers. The sampling process can be initiated either locally, with a

*Reprinted with permission of "Canadian Research" published by MacLean-Hunter Ltd., Toronto, Canada.



*Molded carousel houses 50 minitubes and is the transfer vehicle for samples.*

hand held switch or remotely by a radio transmitter.

On completion of the sampling cycle, the carousel containing the minitubes is removed and returned to the laboratory for analysis of the adsorbed contaminents.

To facilitate analysis, an automated thermal desorption sample injection system was designed and developed by CCAI. This injection system was retrofitted to a commercial gas chromatograph. Control of the analysis cycle can be manually programmed by an operator through a front panel console or, optionally, through a preprogrammed module which can be plugged into the injection system. The output data from the gas chromatograph are manipulated by a commercial minicomputer. A further option, which would permit this minicomputer to control the analysis cycle, may be implemented in the future. This option would be able to predict trends and control the sample injection system accordingly (for example, if the concentration of a particular sample was insignificant, it would be rejected and the next minitube selected).

The technique of thermal desorption permits reuse of the minitubes as contaminants are "flushed out" during analysis. The carousel can be removed from the injection system and immediately replaced in a field sampler for another sampling cycle.

The prototype system has been completed and tested. A further contract to supply production quantities to DRES is expected shortly. A patent application has been initiated by the Department of National Defence and a license will be granted to CCAI for commercial exploitation.

Defence markets (i.e., other NATO countries) are being investigated as well as other applications such as: agricultural (measure herbicide drift downwind of a crop spraying operation), industrial (analyze effluents from industrial processes), and environmental (monitor workplace air quality with respect to worker's health and safety concerns).

Specifications for a commercial version of MASS are being compiled. It is expected that this system will be a simplified version of the defence system. For example, it is likely the commercial version would not require remote initiation of the sampling process. It is also probable that the controller will be an integral part of the sampler rather than a separate package. For those customers who do not wish to commit to the expense of the laboratory analytical system, arrangements will be made to have the analysis performed on a fee-for-service basis by the analytical laboratories of the Saskatchewan Research Council.

This contract was truly a "win-win" situation. It not only solved a difficult problem cost effectively, but indications are that the technology will be successfully transferred to the marketplace nationally and internationally.